Online available since 2011/Jul/04 at www.scientific.net
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doi:10.4028/www.scientific.net/KEM.485.107

The Effect of Carbon Doping on Electrochemical Properties of $LiFePO_4$/C Powders Prepared by Spray Pyrolysis

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Keywords: $LiFePO_4$, olivine structure, carbon, lithium ion battery, spray pyrolysis

Abstract. Spherical $LiFePO_4$/C precursor powders were successfully prepared by spray pyrolysis. Various types of organic compounds such as glycolic acid, malic acid, citric acid, fructose and sucrose were used as carbon sources. X-ray diffraction analysis revealed that the olivine phase was obtained by calcining over 600 °C under an argon (95%)/hydrogen (5%) atmosphere. The particles exhibited a spherical morphology with approximately 1.5 μm. $LiFePO_4$/C cathode derived from sucrose exhibited higher rechargeable capacity and cycle stability. The rechargeable capacity of $LiFePO_4$/C cathode was approximately 154 mAh/g at 1 C. 90% of initial discharge capacity was maintained after 100 cycles.

Introduction

Recently, olivine-type $LiMPO_4$ (M = Fe, Mn, Ni, and Co) has attracted extensive attention due to a relatively high theoretical capacity (170 mAh/g) [1]. $LiFePO_4$ is the most attractive because of its rare-metal free composition, its long plateau during charge and discharge, its good cycle stability at high temperatures. However, the rechargeable capacity was low at high rates because electrical conductivity of $LiFePO_4$ is very low. Therefore, conductive materials such as carbon and metals were added to $LiFePO_4$ in order to enhance its electrical conductivity [2-4]. Spray pyrolysis [5] is a versatile process that is used to synthesize oxide and metal fine powders. The advantages of spray pyrolysis are that it allows to control of the particle size, particle size distribution, and particle morphology. In addition, fine powders with a homogeneous composition can be easily synthesized, because the starting solution components are kept in a mist. In this study, $LiFePO_4$/C powders were prepared by spray pyrolysis using various types of organic compounds. The powder characteristics of them and the Effect of carbon doping on electrochemical properties of $LiFePO_4$/C were investigated.

Experimental procedure

Spray pyrolysis process [6] was used to prepare $LiFePO_4$/C powders. $LiNO_3$, $Fe(NO_3)_3 \cdot 9H_2O$ and H_3PO_4 was used as starting materials. These compounds were dissolved in water at room temperature. The molar ratio of the metal component (Li : Fe : P) was set to 1 : 1 : 1 in the starting solution. The concentration of the solution was 0.25 mol/dm^3. Various types of organic compounds such as glycolic acid, malic acid, citric acid, fructose and sucrose were used as carbon sources. The molar ratio of $LiFePO_4$: C was set to 1 : 12 in the starting solution. The starting solution was misted using an ultrasonic nebulizer at a frequency of 1.6 MHz. Air was used as the carrier gas during the preparation of $LiFePO_4$/C powders. The generated mist were carried to an electric furnace by air carrier gas with a flow rate of 8 dm^3/min and then pyrolyzed at 500 °C. $LiFePO_4$/C precursor powders were continuously collected using cyclone. Furthermore, the precursor powders were calcined over 600 °C in electric furnace under an argon (95%)/hydrogen (5%) atmosphere. The heating and cooling rates were 5 °C/min and 4 °C/min, respectively.

The crystal phase of $LiFePO_4$/C powders and the calcined powders was identified by powder X-ray diffraction (XRD, Shimadzu, XRD-6100) using CuKα radiation. The chemical composition of $LiFePO_4$/C powders was determined by inductively coupled plasma atomic emission spectroscopy

(ICP-AES, SII NanoTechnology, SPS-7800). The particle size, morphology and microstructure of $LiFePO_4$/C powders were determined by using a scanning electron microscope (SEM, JEOL, JSM-6390). In the SEM images, 200 particles were randomly sampled to determine the average particle size of $LiFePO_4$/C powders. The thermal behavior of carbon sources was observed using a thermo gravimetric-differential thermal analysis equipment (TG-DTA, Shimadzu, DTG-60). The carbon content of the $LiFePO_4$/C particles was determined by TG-DTA. Cathodes were prepared using 75 mass% $LiFePO_4$/C powders, 15 mass% acetylene black and 10 mass% fluorine resin. A metal lithium sheet (Honjo chemical) was used as an anode. The celgard (Heist, celgard 2400) was used as a separator. 1mol/dm^3 $LiPF_6$ in ethylene carbonate / 1,2-dimethoxyethane (EC : DEC = 1 : 1, Tomiyama pure chemical) was used as the electrolyte. 2032 coin type cell was built up in globe box under an argon atmosphere. The rechargeable capacity and cycle stability of cathodes were measured with a battery tester (Hosen, BTS2004) at between 2.5V and 4.3V.

Results and discussion

The crystal phase and crystallinity of $LiFePO_4$/C powders were observed by using the XRD. Figure 1 shows the XRD patterns of $LiFePO_4$/C powders prepared by spray pyrolysis of an aqueous solution with the indicated organic compound. These powders were calcined at 750 °C for 3 hrs. From these patterns, it was observed that the diffraction patterns of $LiFePO_4$/C powders were good agreement with olivine phase (space group: Pnma), and other phases were not observed. The crystallinity of $LiFePO_4$/C powders obtained from glycolic acid was similar to that of $LiFePO_4$ powders. On the other hand, the crystallinity of the $LiFePO_4$/C powders obtained from saccharides was relative low. Chemical analysis revealed that the metal component (Li : Fe : P) ratio of the calcined powders was agreement with the starting solution component. The diffraction patterns of carbon were not observed by XRD. This suggested that the carbon contained in $LiFePO_4$/C powders is amorphous and that the presence of carbon does not influence the formation of $LiFePO_4$. TG-DTA analysis showed that the carbon contents of $LiFePO_4$/C powders obtained from glycolic acid, malic acid, citric acid, fructose and sucrose were 0.5 mass%, 2 mass%, 1.5 mass%, 16 mass% and 18 mass%, respectively. The thermal behavior of carbon sources was observed using TG-DTA. The thermal decomposition temperature of organic acid was from 150 to 470 °C. On the other hand, the thermal decomposition temperature of saccharides was from 200 to 650 °C. Therefore, the carbon contents of $LiFePO_4$/C powders obtained from saccharides was rich compared with that of $LiFePO_4$/C powders obtained organic acid. Figure 2 shows the SEM images of $LiFePO_4$ and $LiFePO_4$/C powders obtained from

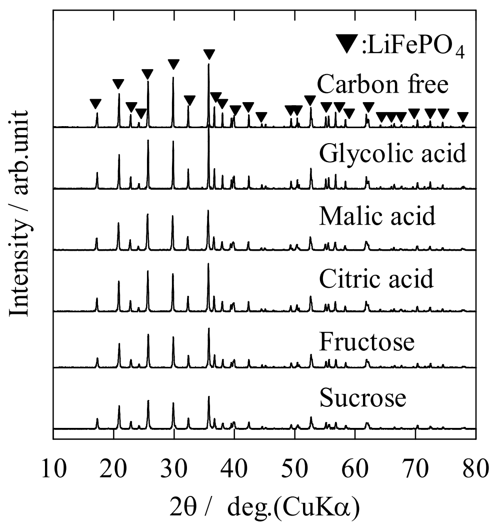


Fig. 1 XRD patterns of $LiFePO_4$ and $LiFePO_4$/C powders calcined at 700 °C for 3 hrs under argon (95%)/hydrogen (5%) atmosphere.

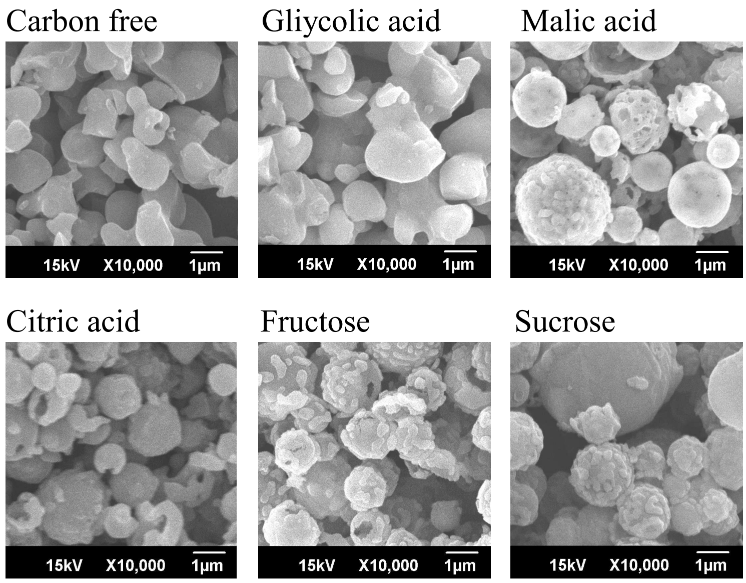
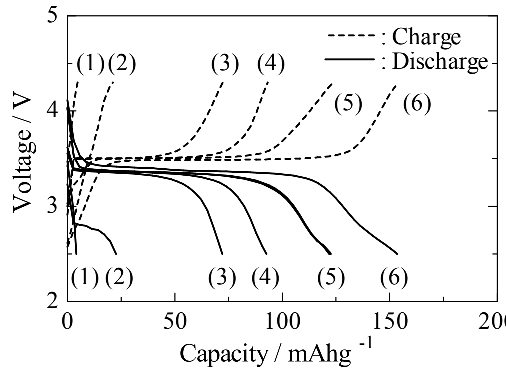


Fig. 2 SEM images of $LiFePO_4$ and $LiFePO_4$/C powders obtained from various types of organic compounds.



(1)Carbon free (2)glycolic acid (3) Malic acid (4) Citric acid (5) Fructose (6) Sucrose

Fig. 3 Rechargeable curves of $LiFePO_4$ and $LiFePO_4$/C cathodes at 1 C.

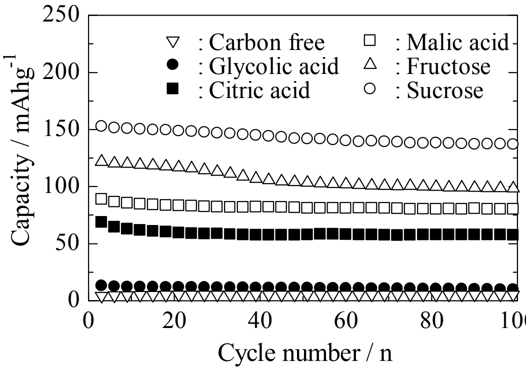
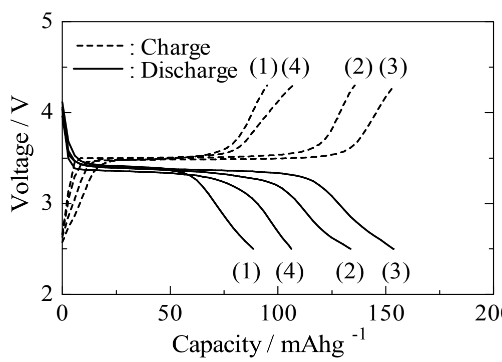


Fig. 4 Cycle performance of $LiFePO_4$/C cathodes at 1 C.

various types of organic compounds. $LiFePO_4$ particles and LiFePO4/C particles obtained from gliycolic acid exhibited an irregular morphology. When the other carbon sources were used, the particles exhibited a spherical morphology with a hollow microstructure and nonaggregated regardless of the types of carbon sources used. This resulted in the drastic decomposition of organic acid in the step of pyrolysis. The average size of $LiFePO_4$ and $LiFePO_4$/C powders was approximately 1.2 μm.

The electrochemical properties of $LiFePO_4$/C as cathode for lithium battery were examined. Figure 3 shows rechargeable curves of $LiFePO_4$/C cathodes obtained from various types of organic compounds at 1 C. A long plateau was observed at approximately 3.5V in each rechargeable curve. The charge and discharge capacities were 154 mAh/g for the $LiFePO_4$/C cathode obtained from sucrose, approximately 158 mAh/g and 148 mAh/g for the $LiFePO_4$/C cathode obtained from fructose, 123 mAh/g for the $LiFePO_4$/C cathode obtained from malic acid, 73 mAh/g for the $LiFePO_4$/C cathode obtained from citric acid, 23 mAh/g for the $LiFePO_4$/C cathode obtained from glycolic acid, and 4 mAh/g for the $LiFePO_4$ cathode, respectively. The rechargeable efficiency was very high regardless of the type of organic compounds. The rechargeable capacity of the $LiFePO_4$/C cathode obtained from sucrose was higher than that obtained from other organic compounds. It is considered that the difference in carbon contents is related to the difference in rechargeable capacities. Figure 4 shows the relation between cycle number and discharge capacity of $LiFePO_4$/C cathodes obtained from various types of organic compounds at 1 C. The discharge capacity decreased with increasing discharge rate.



(1)600 °C (2) 700 °C (3)750 °C (4) 800 °C

Fig. 5 Rechargeable curves of $LiFePO_4$/C cathodes obtained from sucrose at 1 C.

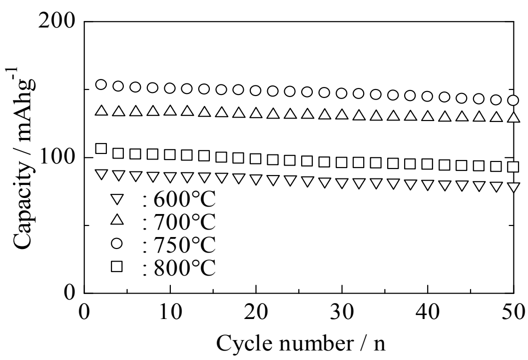


Fig. 6 Cycle performance of $LiFePO_4$/C cathodes obtained from sucrose at 1 C.

The discharge capacity of the $LiFePO_4/C$ cathodes after 100 cycles at 1 C was approximately 90% of the initial discharge capacity regardless of the type of organic compounds. It was found that the $LiFePO_4/C$ cathodes exhibited excellent cycle stability.

Figure 5 shows rechargeable curves of $LiFePO_4/C$ cathodes obtained from sucrose at 1 C. $LiFePO_4/C$ cathodes obtained from sucrose were calcined from 600 °C to 800 °C in electric furnace under an argon (95%)/hydrogen (5%) atmosphere for 3hrs. When $LiFePO_4/C$ cathode was calcined at 750 °C, $LiFePO_4/C$ cathode exhibited the best rechargeable capacity and rechargeable efficiency. Figure 6 shows the relation between cycle number and discharge capacity of $LiFePO_4/C$ cathodes obtained from sucrose at 1 C. After 50 cycles, approximately 90% of initial discharge capacity was maintained regardless of the calcination temperature. Figure 7 shows the relation between cycle number and discharge capacity of $LiFePO_4/C$ cathodes obtained from sucrose and calcined at various time at 1 C. $LiFePO_4/C$ cathodes were calcined at 750 °C. When $LiFePO_4/C$ cathode was calcined for 1 hr, the discharge capacity of the $LiFePO_4/C$ cathode after 100 cycles was approximately 95% of the initial discharge capacity. On the other hand, the discharge capacity of the $LiFePO_4/C$ cathodes calcined for other time after 100 cycles was approximately 90% of the initial discharge capacity. However, the discharge capacity of these cathodes was high compared with the discharge capacity of $LiFePO_4/C$ cathode calcined for 1 hr.

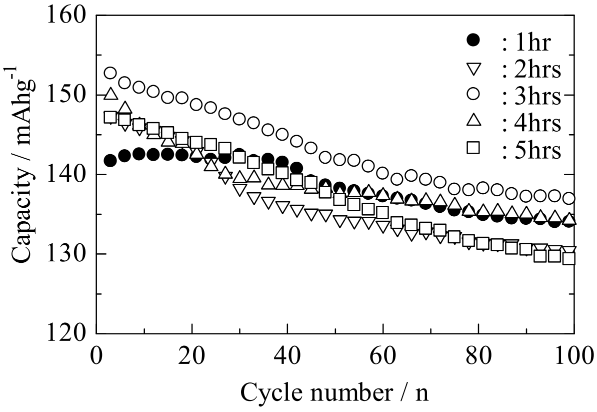


Fig. 7 Cycle performance of $LiFePO_4/C$ cathodes calcined at various time at 1 C.

Conclusion

$LiFePO_4/C$ powders were prepared by spray pyrolysis using an aqueous solution of organic compounds. XRD revealed that the diffraction peaks of all samples were agreement with olivine phase. $LiFePO_4/C$ powders were a spherical morphology with 1.2 μm and nonaggregation. The calcined powders have uniform chemical composition. The electrochemical properties of $LiFePO_4$ were improved by addition of carbon. The addition of sucrose led to highest discharge capacity of $LiFePO_4/C$.The discharge capacity of $LiFePO_4/C$ was 154 mAh/g at 1 C. The rechargeable capacity changed by changing the calcination temperature and the calcination time, but the stability of cycle performance was maintained. The electrochemical measurement revealed that $LiFePO_4/C$ cathodes obtained from sucrose had the higher rechargeable capacity and stable cycle performance.

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Electroceramics in Japan XIV
doi:10.4028/www.scientific.net/KEM.485

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doi:10.4028/www.scientific.net/KEM.485.107